Title: DEVELOPMENT OF HIGH ACTIVITY, COAL-DERIVED, PROMOTED CATALYTIC SYSTEMS FOR NO_X REDUCTION AT LOW TEMPERATURES

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ABSTRACT

OBJECTIVES

This project is directed at an investigation of catalytic NO_X reduction mechanisms on coal-derived, activated carbon supports at low temperatures (300°C-450°C). Promoted carbon systems offer some potentially significant advantages for heterogeneous NO_X reduction. These include: low cost; high activity at low temperatures, to minimize carbon loss; oxygen resistance; and a support material which can be engineered with respect to porosity, transport and catalyst dispersion characteristics.

The project is currently focused on two promising systems - potassium; and Co/Ni-rare earth oxide-Pt, which have both been shown to be effective for NO reduction at low temperatures, with low carbon loss. In particular, the focus is on the investigation of : (1) a novel, “two-stage” process for the complete reduction of NO to N_2 and O_2 *via* N_2O as an intermediate; and (2) the use of H_2 and CO reducing agents in conjunction with the promoted carbon systems.

In order to develop and optimize these approaches, however, the fundamental mechanisms responsible

for NO_X reduction in these catalytic systems must be better understood and quantified. In this regard, various techniques that have been developed in our laboratory to investigate carbon reactivity will be applied to accomplish this objective. These include temperature programmed reaction (TPR), and post-reaction/chemisorption temperature programmed desorption (TPD) methods.

ACCOMPLISHMENTS TO DATE

MS-TGA Studies: A MS-TGA (mass spectrometric-thermogravimetric analysis) apparatus, which is one of the primary instruments to be used in these studies, has been modified to the specific requirements of this project. A NO_X chemiluminescence analyzer has been added to the instrument to monitor NO_X concentrations in the feed and product streams. In addition, the computer control and data acquisition system has been updated and modified to accommodate the specific types of experiments required.

A packed bed reactor/gas flow system has been assembled for performing reactivity studies. This system employs a gas calibration/mixing system for varying NO and CO concentrations in the feed gas to the packed bed, a NO_X chemiluminescence analyzer, and a quadrupole mass spectrometer. This system is required for steady-state reactivity studies, as well as mechanistic studies on the effects of NO and CO in the gas phase on intermediate oxygen surface complex populations on the carbon substrates.

Both these systems have been used to investigate the effects of NO and CO in the gas phase on intermediate oxygen surface complex populations on the carbon have been investigated. Phenolic resin char was oxidized in a packed bed reactor, with NO alone, CO alone, and NO+CO in 100 ml/min of helium for 2h at 800°C. Samples of this carbon bed material were then subject to temperature programmed desorption in the MS-TGA apparatus at 70K/min in flowing ultrahigh purity helium. With just NO in the flow, relatively little surface oxygen was evolved at temperatures less than 800°C, with a maximum centered at about 980°C. With only CO in the flow, the carbon surface accumulated considerably more oxygen, especially below 800° C, and no maximum was observed, with CO evolution still increasing at the maximum temperature. This additional surface oxygen is attributable to direct CO chemisorption, and perhaps some reverse Boudouard reaction. When both NO and CO were fed together, however, the oxygen surface complex population was observed to decrease to its lowest levels and the maximum in the evolution rate was shifted up to about 1100°C. These results suggest that CO participates in the reduction of NO *via* reaction with oxygen surface complexes. These studies are intended to establish the mechanism of gas phase reducing agents on heterogeneous NO reduction.

Work has continued on the application of contrast matching, small angle neutron scattering to the characterization and development of char porosity. Contrast matching with perdeuterated toluene has been used to discriminate between inaccessible and inaccessible porosity in Pittsburgh #8 coal char and phenolic resin char. This technique is being investigated from the point of view of porosity characterization of the carbon support materials for NO_X reduction systems.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- Hall, P.J., Antxustegi, M.M., and Calo, J.M., "Development of Porosity in Pittsburgh No. 8 Coal Char As Investigated by Contrast-Matching Small Angle Neutron Scattering and Gas Adsorption Techniques," *Energy & Fuels*, **12,** 542-546, 1998.
- Antxustegi, M.M., Hall, P.J., and Calo, J.M., "The Use of Contrast Matching Small Angle Neutron Scattering Techniques to Monitor Closed Porosity in Carbons," *J. Coll. Intf. Sci.* **202**, 490-498, 1998.The Role of Surface Area in the NO-Carbon Reaction
- Calo, J.M., Suuberg, E.M., Aarna, I., Linares-Solano A., Salinas-Martínez de Lecea, C., and M.J. Illán-Goméz, M.J.," The Role of Surface Area in the NO-Carbon Reaction," *Energy & Fuels*, in press, May 17, 1999.

Conference Presentations

- Calo, J.M., Hall, P.J., Brown, S., Fernandez, J., and Antxustegi, M., "Carbon Porosity Development *Via* Small Angle Scattering," to be presented at Twenty-Fourth Biennial Conference on Carbon, Charleston, South Carolina, July, 1999.

Students Supported Under This Grant

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